# Chitosan and Surfactant Impregnated Chitosan Beads for Removal of Textile Dye Brilliant Black BN from Aqueous Solution

Shadeera Rouf, M.Nagapadma

**Abstract**

Chitosan and CTAB (Cetyl Trimethyl Ammonium bromide) impregnated chitosan beads were prepared and used for the removal of dye Brilliant black BN from aqueous solution. Batch experiments were conducted to study the effect of CTAB concentration, contact time, agitation speed, adsorbent dosage, initial dye concentration and pH. CTAB concentration was varied from 0.01% (v/v) to 0.04% (v/v) and maximum adsorption capacity was attained at 0.02%. Adsorption was initially rapid and attained equilibrium after 5 hours. Adsorption capacity increased with increase in initial dye concentration and decreased with increase in pH. Equilibrium adsorption data were analyzed using Langmuir and Freundlich models and data agreed very well with Freundlich isotherm. Kinetic data showed better fit to pseudo second order rate model than pseudo first order rate model.

**Key words:** Chitosan beads: Brilliant Black BN: CTAB: Batch studies: Langmuir model: Freundlich model

## 1. INTRODUCTION

Chitosan is a linear polysaccharide composed of randomly distributed β-(1-4) - linked D-glucosamine and N-acetyl-D-glucosamine. It is obtained by partial deacetylation of chitin which is the second largest polymer after cellulose. Chitin is a white, hard, inelastic, nitrogenous polysaccharide found in the cell walls of fungi. Chitin is also a major component in the exoskeleton of arthropods such as crustaceans and insects. Chitin and chitosan show excellent properties like biodegradability, biocompatibility, non-toxicity and adsorption [1]. These properties depend on the amount of protonated amino groups present in the polymeric chain. Chitosan has proved to be effective for the removal of metal ions and dyes. A dye is a colored substance that has an affinity to the substrate to which it is applied. Today there are more than 10,000 dyes available commercially. Synthetic dyestuffs widely exist in the effluents of industries such as textiles, printing, paper, plastics and leather. Colored industrial effluent contains many varieties of synthetic dyes including azo dyes which are mostly toxic and mutagenic, and even carcinogenic in nature [2].In the present work, chitosan was used for the removal of dye Brilliant Black BN. Brilliant Black BN is an azo dye which is used in textile, paper and pulp, leather industries etc. It is a benzidine based anionic diazo dye. Brilliant Black BN has

metabolized to benzidine, a human carcinogen. Synthetic dyes such as Brilliant Black BN are very difficult to remove because of their complex aromatic structure, which provides them physical, chemical, thermal and optical stability [3]. Chitosan can be used as an effective adsorbent for the removal of azo dyes. Chitin and chitosan are now produced in India commercially. Chitosan is available commercially as flakes or as powder. Though chitosan has been proved to be effective in adsorption, the adsorption capacity of chitosan has not been realized to a satisfying level because chitosan powder and flakes crumbles and swells and because of this, it is very difficult to pack chitosan in adsorption column [4]. The regeneration of chitosan powder is also difficult. To overcome these difficulties chitosan can be modified into beads and the adsorption capacity of chitosan can be increased. Recently, chitosan modified with a cationic surfactant CTAB (Cetyl Trimethyl Ammonium Bromide) has proved to be effective for removal of the dye Congo Red [5]. But the time required for production of beads were much longer and took removal of the dye Congo Red. But the time required for production of beads were much longer and took above twenty four hours for completion. In the present work, chitosan beads were prepared and modified with CTAB in a simpler way to study removal of azo dye Brilliant Black BN. Batch studies were conducted to study the efficiency of chitosan beads for dye removal. The effect of CTAB concentration, contact time, agitation speed, adsorbent dosage, pH and initial dye concentration were investigated.

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been known to cause allergic reaction and to be

## 2. METHODS

## 2.1. Preparation of Chitosan Beads

Chitosan (90% de acetylated) was purchased from marine biotech Ltd, Kerala. The chemicals such as acetic acid (Fisher Scientific), NaOH (Fisher Scientific) and surfactant CTAB (S.D.Fine Chem Ltd) were purchased locally. Chitosan beads were prepared by dissolving 2 gm chitosan in 60 ml 5 % acetic acid. Solution was stirred for some time in a magnetic stirrer and added drop wise to 500 ml 0.5 M NaOH. Beads were washed thoroughly with distilled water and stored in distilled water until used.

## 2.2. Preparation of Chitosan Beads Impregnated with CTAB

1% (wt/v) CTAB solution was prepared by dissolving 1 gm CTAB in 100 ml distilled water. 0.01%, 0.02%, 0.03% and 0.04% CTAB chitosan beads were prepared by dissolving required amount of CTAB solution to 2 gm chitosan. The volume was made up to 60 ml using 5% (v/v) acetic acid. The solution was stirred in a magnetic stirrer for twenty minutes. After stirring, solution was added drop wise to 500 ml NaOH using syringe. Beads were washed thoroughly with distilled water and stored in distilled under used.

## 2.3. Batch Adsorption Studies

Batch studies were carried out on orbitek shaker at 160 rpm using 250 ml conical flasks containing 0.5 mg chitosan beads and 50 ml dye solution of required concentration and pH. The effect of CTAB concentration was studied by varying concentration of CTAB in chitosan beads from 0.01% to 0.04% (C0=20 mg/l). The effect of contact time on dye removal was studied to determine the time taken by chitosan beads (CB) and chitosan-CTAB beads (CB-CTAB) to reach equilibrium at pH 7 and C0 was fixed at 20 mg/l. The concentration of dye after treatment was determined after every one hour and the experiment was continued for 7 hours. The effect of agitation speed was studied by varying the agitation speed from 120 rpm to 200 rpm. The effect of adsorbent dosage was studied by varying the adsorbent dosage from 0.25 gm to 1.5 gm. The influence of pH on dye removal was studied by varying the pH from 4 to 9 using 0.1 N NaOH and 0.1 N HCl. Equilibrium adsorption studies were carried out with different initial concentration of Brilliant Black BN ( 2 -100 mg/l) at pH 4. The concentration of dye before and after treatment was analyzed using UV-VIS spectrophotometer SL159 by measuring absorbance at 576nm. The amount of BBN adsorbed was determined using the following mass balance equation:

$$q_e = \frac{C_o - C_e}{W} V \qquad (1)$$

Where, qe is the adsorption capacity mg/gm; Co is the initial dye concentration, ppm; Ce is the equilibrium dye concentration, ppm; V is the volume of dye solution, ml and W is the dry weight of adsorbent, gm.

# 3. RESULTS AND DISCUSSION

## 3.1. Characterization of Chitosan Beads

The FTIR spectra of chitosan beads before and after impregnating CTAB is shown in figure 1. The spectrum of chitosan beads CB were characterized by bands at 1559.26 cm-1 (-N-H- bend of primary amines), the adsorption sites and 1318.98 cm-1 ( -C-O- stretch of alcohol). The spectrum of chitosan beads impregnated with CTAB are characterized by bands at1558.10 cm-1 (-N-H- bend of primary amines), the adsorption sites 1300.84 cm-1 (-C-O- stretch of alcohol), 1652.82 cm-1 (-N-H- bend of primary amines), 1241.59 cm-1(-C-H- Wag of alkyl halide), 846.04 cm-1 (-N-H Wag of primary and secondary amines) and 429.19 cm-1 (-C-Br stretch of alkyl halide), responsible for hydrophobic interaction. The difference in composition of beads confirms that CTAB has been successfully impregnated to the beads.

## 3.2. Effect of CTAB Concentration

The effect of CTAB concentration on dye removal is shown in figure 2. It can be seen that the adsorption capacity increased with increase in CTAB concentration from 0.01% to 0.02 %. Further increase in CTAB concentration decreased adsorption capacity. The increase in adsorption capacity with increase in CTAB concentration is due to the increased hydrophobic interaction between the hydrophobic moieties of CTAB and the hydrophobic moieties of dyes. The increased positive charge due to the positively charged head group of CTAB might also have contributed to the increased adsorption capacity. Above 0.02 % CTAB concentration, foam formation occurred. The beads formed were less rigid and adsorption capacity was lesser. But the adsorption capacity of beads with CTAB was higher compared to the beads without CTAB. So 0.02 % CTAB concentration was taken as the optimum concentration for adsorption.

## 3.3. Effect of Contact Time

Variation of adsorption capacity with contact time is shown in figure 3. It can be observed that adsorption was initially rapid and increased considerably with increase in contact time from 0 to 5 hours for both beads. Further increase in contact time did not influence adsorption considerably. Thus equilibrium was reached after five hours.

## 3.4. Effect of Agitation Speed

The influence of agitation speed on adsorption is shown in figure 4. The figure shows that as agitation speed increased from 120 rpm to 160 rpm, there was a significant increase in adsorption capacity. Further increase in agitation speed did not have significant effect on dye removal. Lower adsorption capacity at lower speed was due to the poor interaction between adsorbate and adsorbent. As the speed reached 160 rpm, there was sufficient increase in adsorption capacity. As the speed was increased above 160 rpm, adsorption capacity did not vary significantly. Thus, 160 rpm is the optimum agitation speed for adsorption.
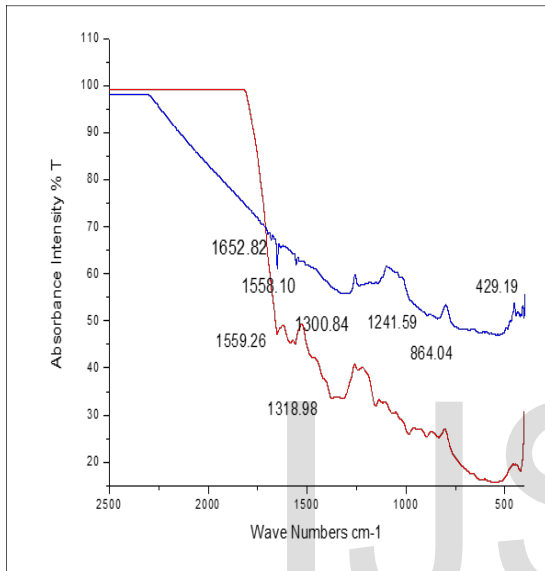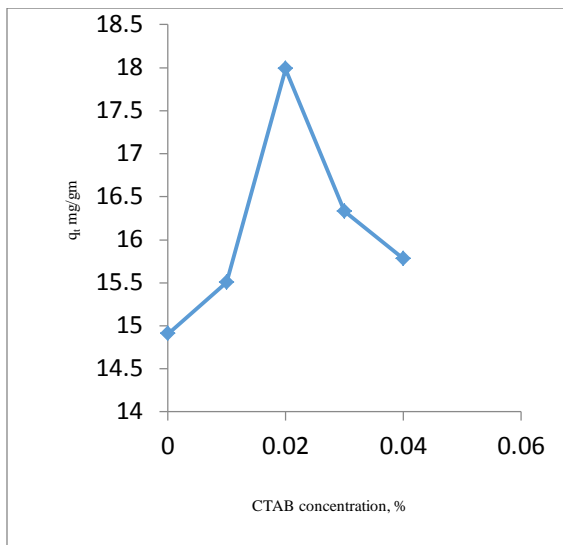


**Fig. 1:** FTIR analysis of chitosan beads



. **Fig. 2:** Effect of CTAB concentration on adsorption capacity
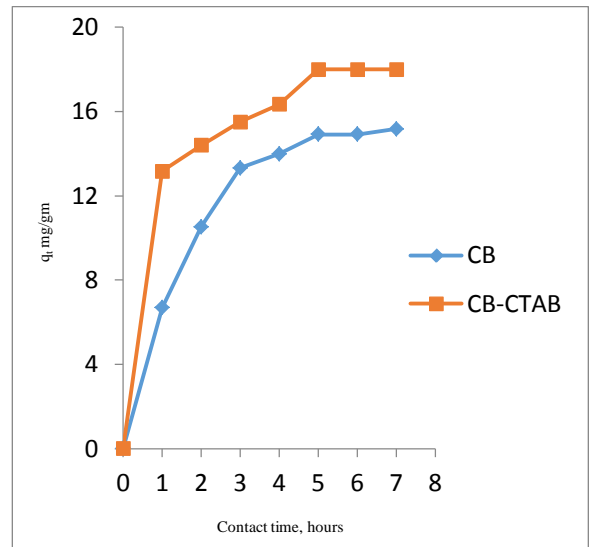


**Fig. 3:** Effect of contact time on adsorption capacity

## 3.5. Effect of Adsorbent Dosage

The effect of adsorbent dosage on adsorption is shown in figure 5. Percentage removal of dye increased from 48.55 % to 77. 51% using chitosan beads and from 64.41 % to 89.93 % using chitosan beads impregnated with CTAB. It can be seen that 1 gram beads modified with CTAB and 1.5 grams of normal chitosan beads were showing almost same percentage dye removal. It can be concluded that modification of beads resulted in less adsorbent requirement.
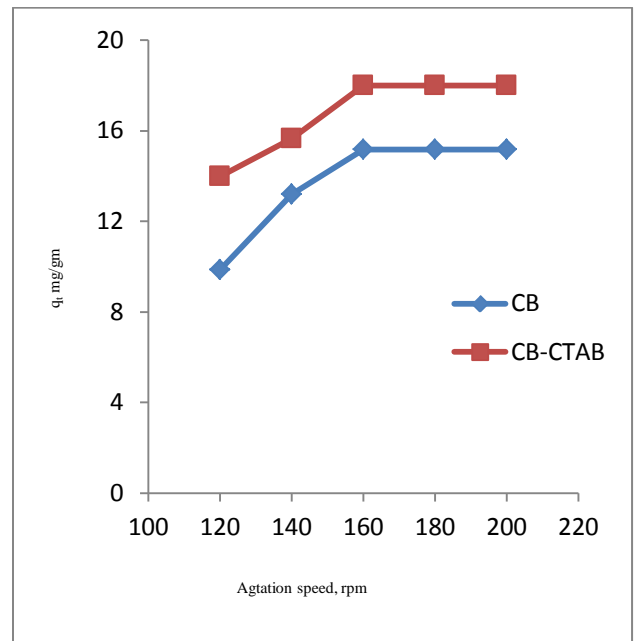


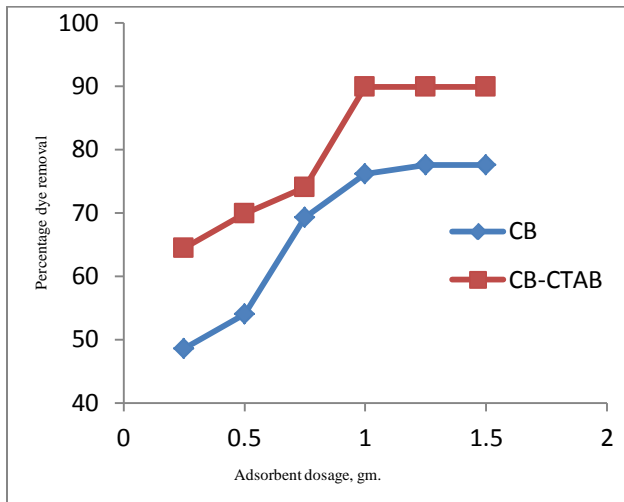**Fig. 4:** Effect of agitation speed on adsorption capacity

**Fig. 5**: Effect of adsorbent dosage on dye removal



**Fig. 6:**:Effect of pH on adsorption capacity

## 3.6. Effect of pH

The results revealed that pH influences dye removal strongly. The effect of pH on dye removal is shown in figure 6. The figure shows that higher adsorption occurred at lower pH. As the pH increased from 4 to 9, there was a considerable decrease in adsorption capacity. This is due to the fact that at lower pH more protonated amino groups will be available. The trend was same for both beads and at every pH, CTAB impregnated beads were showing higher adsorption.

## 3.7. Effect of Initial Dye Concentration

The effect of initial dye concentration on dye removal is shown in figure 7 and 8. Results showed that adsorption capacity increased with increase in dye concentration. This was because, concentration difference was the driving force for adsorption and higher concentration, driving force increased. At every concentration, CTAB modified beads had higher adsorption capacity. Also, the adsorption capacity of CTAB impregnated beads increased with increase in adsorption capacity. At higher concentration, adsorption capacities of CTAB beads were almost 20 % greater as compared to beads without CTAB. That at higher dye concentration, hydrophobic interaction between dye and CTAB was higher.
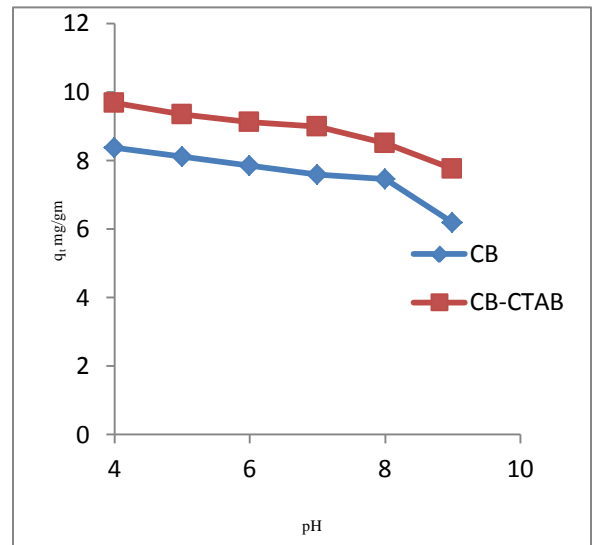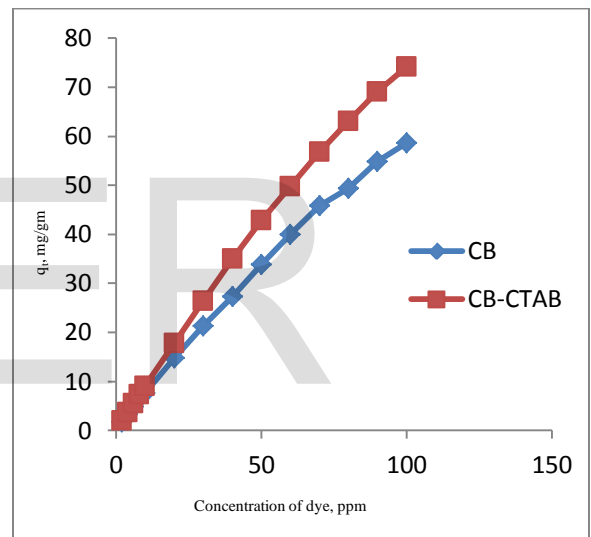


**Fig. 7:** effect of initial dye concentration on adsorption capacity

Although adsorption capacity increased with increase in dye concentration, the corresponding percentage removal of dye decreased considerably. This can be attributed to the fact that, at higher concentration, active sites were filled rapidly. This resulted in faster saturation of the adsorbent and decreased reaction sites available for adsorption. Thus, percentage dye removal increased with increase in initial dye concentration.
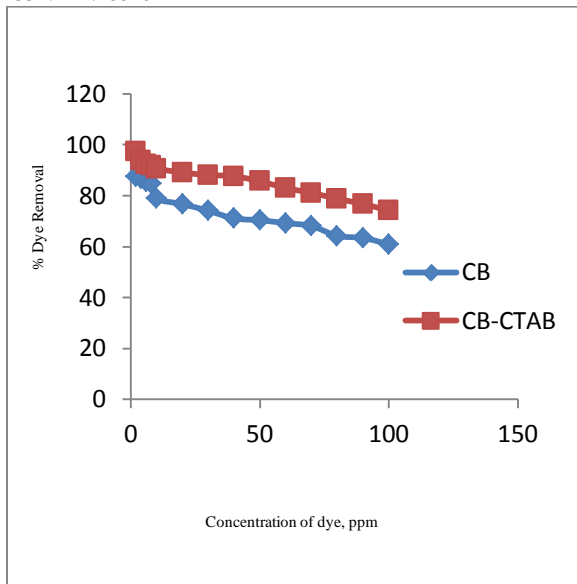
**Fig. 8:** Effect of initial dye concentration on

percentage dye removal

### 3.5. Equilibrium Adsorption Isotherm

Equilibrium adsorption isotherm model is fundamental in describing the interactive behavior between adsorbent and adsorbate. The distribution of the adsorbate between the adsorbent and the liquid phase is a measure of the position of equilibrium in the adsorption process and is expressed by isotherm models. In the present study, equilibrium data were analyzed using Langmuir and Freundlich isotherm models. Langmuir isotherm model assumes monolayer adsorption of adsorbate on a homogeneous surface of adsorbent. It is valid for adsorption onto a surface with a finite number of identical adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface. The linearized form of Langmuir model is:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + a_L \frac{C_e}{K_L} \qquad (2)$$

Where, $C_e$ is the equilibrium dye concentration, ppm; $q_e$ is equilibrium dye concentration on the adsorbent, mg/gm; $a_L$ is Langmuir constant, 1/mg; $K_L$ is Langmuir constant, 1/gm. $a_L$ and $k_L$ are determined from the slope and intercept of the plot of $C_e/q_e$ versus $C_e$

The maximum adsorption capacity $Q_o$ (mg/gm) is given as $Q_o = K_L/a_L$

The most important feature of Langmuir isotherm can be expressed in terms of a dimensionless constant, $R_L$ which is given by the following equation:

$$R_L = \frac{1}{1 + a_L C_o} \qquad (3)$$

$R_L$ values in the range 0 to 1 indicate favorable adsorption. It is suggested that the adsorption is unfavorable if $R_L$ is greater than 1.

Freundlich model is usually adopted for heterogeneous adsorption. It is an empirical equation which describes the surface heterogeneity of the adsorbent. This model considers multi-layer adsorption with a heterogeneous energetic distribution of active sites which is accompanied by interaction between adsorbed molecules. The linear form of Freundlich equation is:

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \qquad (4)$$

Where, $K_F$ is Freundlich constant, 1/gm; n is Freundlich constant; $q_e$ is equilibrium adsorption capacity, mg/gm; $C_e$ is equilibrium dye concentration, ppm.
$K_F$ is related to extend of adsorption 1/n is related to the adsorption intensity and varies with the heterogeneity of the material. n represents the mutual interaction of the adsorbed species. Usually, the experimental values of n are greater than unity which means that the forces of interaction between adsorbed molecules are repulsive. If the value of n is close to zero, it implies that the system more heterogeneous. The values of 1/n and $K_F$ are calculated from the slope and intercept of the plot of ln $q_e$ versus ln $C_e$.

Equilibrium adsorption data analyzed by Langmuir model is shown in figures 9 and 10. The values of Langmuir constant and maximum adsorption capacity determined by model are given in table 1.
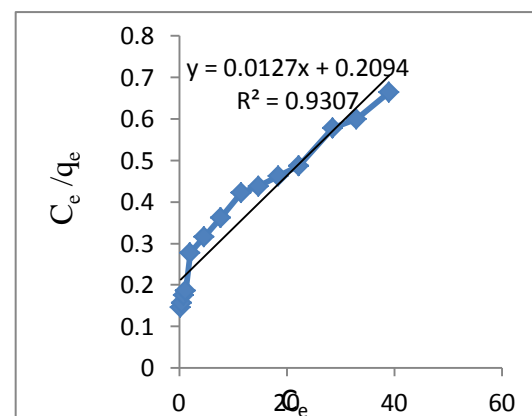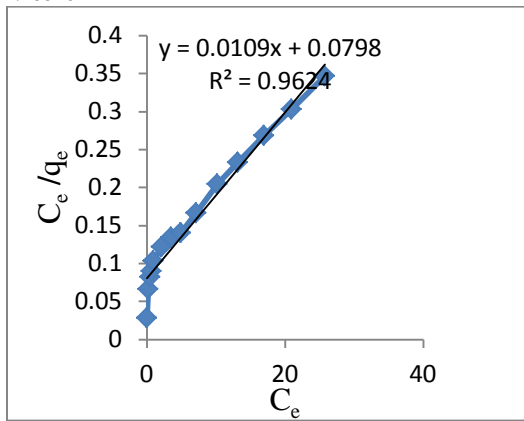


**Fig. 9:** Langmuir plot for CB
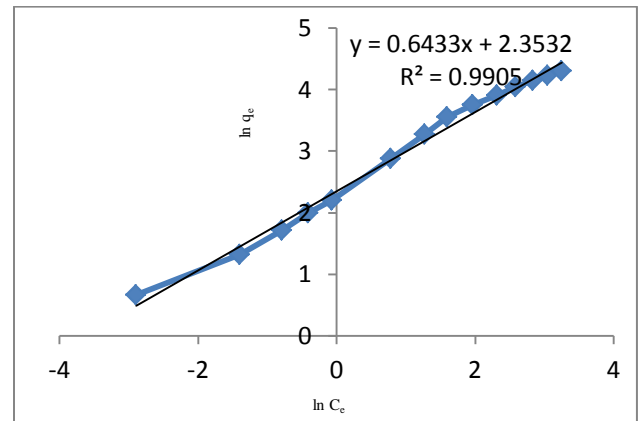
**Fig. 10**: Langmuir plot for CB-CTAB

The value of maximum monolayer adsorption capacity from Langmuir model for CTAB impregnated chitosan beads is about 20 % more than that of unmodified beads. So, modification of beads with CTAB has resulted in an increase in adsorption capacity.

The Freundlich plot and corresponding Freundlich constants are given in figures 11 and 12 and table 2. The Freundlich constants related to the adsorption intensity and extend of adsorption is higher for beads modified with CTAB. On comparing the values of $R^2$ with that of Langmuir isotherm, it can be concluded that the system is best described by Freundlich isotherm model with $R^2$ equal to 0.99.

TABLE 1
Langmuir constants

| Bead | $K_L$ 1/gm | $a_L$ 1/mg | $Q_0$ mg/gm | $R^2$ |
|---|---|---|---|---|
| CB | 4.77 | 0.06 | 78.13 | 0.93 |
| CB-CTAB | 12.53 | 0.13 | 92.13 | 0.96 |



**Fig. 11:** Freundlich plot for CB



**Fig. 12:** Freundlich plot for CB-CTAB

TABLE 2
Freundlich constants

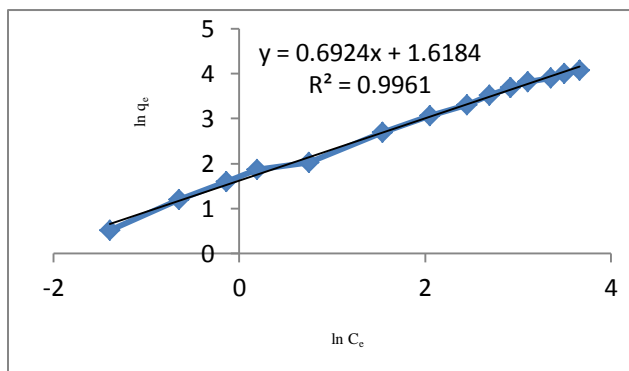| Bead | $K_F$ 1/gm | n | $R^2$ |
|---|---|---|---|
| CB | 1.44 | 10.04 | 0.99 |
| CB-CTAB | 1.55 | 10.51 | 0.99 |

The Freundlich constants related to the adsorption intensity and extend of adsorption is higher for beads modified with CTAB. On comparing the values of $R^2$ with that of Langmuir isotherm, it can be concluded that the system is best described by Freundlich isotherm model with $R^2$ equal to 0.99.

### 3.6. Kinetics of Adsorption

Studying kinetics of adsorption is very important for designing adsorption systems and is required for selecting optimum operating conditions for batch adsorption study. To investigate the adsorption kinetics of Brilliant Black BN on chitosan beads and chitosan beads impregnated with CTAB, pseudo first order and pseudo second order models were used in this study.

The linear form of pseudo first order rate equation is:

$$\log(q_e - q_t) = \log q_{e(cal)} - \frac{k_1 t}{2.303} \qquad (5)$$

Where, $q_e$ is the mount of dye adsorbed at equilibrium, mg/gm; $q_t$ is the mount of dye adsorbed at time t, mg/gm; $k_1$ is the rate constant, 1/min; $q_{e\ (cal)}$ is the calculated adsorption capacity, mg/gm.

The values of $k_1$ and $q_{e\ (cal)}$ were obtained from the slope and intercept of log $(q_e - q_t)$ versus t.

The linearized form of pseudo second order rate equation is given as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_{e(cal)}} \qquad (6)$$

Where, $q_t$ is the amount of dye adsorbed at time t, mg/gm.; h is the initial adsorption rate, (mg/gm.min).

The value of $q_{e\ (cal)}$ and h are obtained from the slope and intercept of $t/q_t$ versus t

The value of pseudo second order rate constant is given by the following equation:

$$h = k_2 q_{e\ (cal)}{}^2 \qquad (7)$$

Where, $k_2$ is Pseudo second order rate constant, g/mg.min.

The pseudo first order and pseudo second order kinetic constants determined from batch kinetic studies are given in the following tables. The corresponding kinetic plots are also shown in figures 13 and 14.
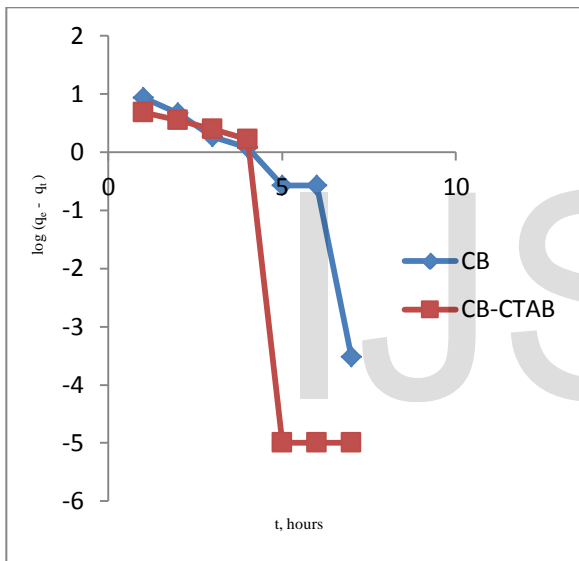


**Fig. 14:** Pseudo second order plot for BBN



**Fig. 13:** Pseudo first order plot for BBN

TABLE 3
Pseudo first order constants for BBN

| Bead | $K_1$ 1/hr | $q_e$ mg/gm | $R^2$ |
|---|---|---|---|
| CB | 1.37 | 98.53 | 0.72 |
| CB-CTAB | 2.75 | 823.00 | 0.78 |

TABLE 4
Pseudo second order rate constants for BBN

| Bead | $K_2$ gm/mg. hr | Q, mg/g m | h mg/gm. hr | $R^2$ |
|---|---|---|---|---|
| CB | 0.03 | 19.04 | 12.04 | 0.99 |
| CB-CTAB | 0.07 | 19.80 | 29.06 | 0.99 |

The values of $R^2$ indicate that adsorption of Brilliant Black BN on chitosan beads follows pseudo second order kinetics. The pseudo second order rate constant is higher for modified beads which indicates higher rate of mass transfer for modified beads. The value of initial adsorption rate, h is also higher for modified beads.

## 5. Conclusion

In the present work, experiments were carried out to study azo dye removal from aqueous solutions using chitosan beads and chitosan beads impregnated with CTAB. Results indicate that the adsorption capacity increased on modifying chitosan beads with CTAB. 0.02 % CTAB concentration has shown highest adsorption capacity. Comparative studies were carried out in batch mode to study the effect of contact time, agitation speed, adsorbent dosage, initial dye concentration and pH. The results showed that at every conditions, CTAB impregnated beads had higher adsorption capacity than chitosan beads. Equilibrium was reached after 5 hours. Adsorption capacity increased with increase in initial dye concentration and percentage dye removal decreased with increase in concentration of dye. Adsorption was higher at lower pH for both chitosan beads and chitosan beads impregnated

with CTAB. Equilibrium isotherm data were described well with Freundlich isotherm model. Adsorption followed pseudo second order kinetics and second order rate constant was higher for modified chitosan beads which indicated a higher rate of mass transfer.

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